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* * * * * Welcome to STN International * * * * *

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NEWS	2	OCT 02	CA/CAPplus enhanced with pre-1907 records from Chemisches Zentralblatt
NEWS	3	OCT 19	BEILSTEIN updated with new compounds
NEWS	4	NOV 15	Derwent Indian patent publication number format enhanced
NEWS	5	NOV 19	WPIX enhanced with XML display format
NEWS	6	NOV 30	ICSD reloaded with enhancements
NEWS	7	DEC 04	LINPADOCDB now available on STN
NEWS	8	DEC 14	BEILSTEIN pricing structure to change
NEWS	9	DEC 17	USPATOLD added to additional database clusters
NEWS	10	DEC 17	IMSDRUGCONF removed from database clusters and STN
NEWS	11	DEC 17	DGENE now includes more than 10 million sequences
NEWS	12	DEC 17	TOXCENTER enhanced with 2008 MeSH vocabulary in MEDLINE segment
NEWS	13	DEC 17	MEDLINE and LMEDLINE updated with 2008 MeSH vocabulary
NEWS	14	DEC 17	CA/CAPplus enhanced with new custom IPC display formats
NEWS	15	DEC 17	STN Viewer enhanced with full-text patent content from USPATOLD
NEWS	16	JAN 02	STN pricing information for 2008 now available
NEWS	17	JAN 16	CAS patent coverage enhanced to include exemplified prophetic substances
NEWS	18	JAN 28	USPATFULL, USPAT2, and USPATOLD enhanced with new custom IPC display formats
NEWS	19	JAN 28	MARPAT searching enhanced
NEWS	20	JAN 28	USGENE now provides USPTO sequence data within 3 days of publication
NEWS	21	JAN 28	TOXCENTER enhanced with reloaded MEDLINE segment
NEWS	22	JAN 28	MEDLINE and LMEDLINE reloaded with enhancements
NEWS	23	FEB 08	STN Express, Version 8.3, now available
NEWS	24	FEB 20	PCI now available as a replacement to DPCI
NEWS	25	FEB 25	IFIREF reloaded with enhancements
NEWS	26	FEB 25	IMSPRODUCT reloaded with enhancements
NEWS	27	FEB 29	WPINDEX/WPIDS/WPIX enhanced with ECLA and current U.S. National Patent Classification

NEWS EXPRESS FEBRUARY 08 CURRENT WINDOWS VERSION IS V8.3,
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* * * * * STN Columbus * * * * *

FILE 'HOME' ENTERED AT 19:43:42 ON 25 MAR 2008

=> file caplus

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.21	0.21

FILE 'CAPLUS' ENTERED AT 19:44:17 ON 25 MAR 2008

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FILE COVERS 1907 - 25 Mar 2008 VOL 148 ISS 13

FILE LAST UPDATED: 24 Mar 2008 (20080324/ED)

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=> s olefin and distillation

106943 OLEFIN
105121 OLEFINS
162727 OLEFIN
(OLEFIN OR OLEFINS)
62318 DISTILLATION
433 DISTILLATIONS
62477 DISTILLATION
(DISTILLATION OR DISTILLATIONS)
180829 DISTN
1822 DISTNS
181581 DISTN
(DISTN OR DISTNS)
201674 DISTILLATION
(DISTILLATION OR DISTN)
L1 4990 OLEFIN AND DISTILLATION

=> s l1 and propane and (propene or proylene)

85100 PROPANE
1133 PROPANES
85677 PROPANE
(PROPANE OR PROPANES)
76190 PROPENE

783 PROPENES
76528 PROPENE
 (PROPENE OR PROPENES)
12 PROYLENE
L2 149 L1 AND PROPANE AND (PROPENE OR PROYLENE)

=> s 12 and (epoxidation or epoxide)
15102 EPOXIDATION
249 EPOXIDATIONS
15136 EPOXIDATION
 (EPOXIDATION OR EPOXIDATIONS)
26780 EPOXIDN
582 EPOXIDNS
26871 EPOXIDN
 (EPOXIDN OR EPOXIDNS)
28644 EPOXIDATION
 (EPOXIDATION OR EPOXIDN)
51094 EPOXIDE
29536 EPOXIDES
66571 EPOXIDE
 (EPOXIDE OR EPOXIDES)
L3 6 L2 AND (EPOXIDATION OR EPOXIDE)

=> d 13 1-6 abs ibib

L3 ANSWER 1 OF 6 CAPLUS COPYRIGHT 2008 ACS on STN
AB Procedure, for the continuous recycling an off-gas flow containing an unreacted olefin resulting by oxidation of olefins with hydroperoxides, includes following steps (1) compaction and cooling the off-gas flow, (2) separation the olefin from the off-gas flow by distillation, and (3) epoxidn. of the separated olefin with a hydroperoxide. The procedure is especially useful for epoxidn. of propene to propene oxide, whereby the off-gas flow contains propene and propane.

ACCESSION NUMBER: 2004:367231 CAPLUS
DOCUMENT NUMBER: 140:357189
TITLE: Procedure for the continuous recycling an unreacted olefin resulting by oxidation of olefins with hydroperoxides by compaction and pressure distillation
PATENT ASSIGNEE(S): BASF AG, Germany
SOURCE: Ger. Offen., 6 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10249378	A1	20040506	DE 2002-10249378	20021023
CA 2503449	A1	20040506	CA 2003-2503449	20031023
WO 2004037802	A1	20040506	WO 2003-EP11736	20031023
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR,			

BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
 AU 2003278127 A1 20040513 AU 2003-278127 20031023
 EP 1558596 A1 20050803 EP 2003-769439 20031023
 R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
 IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK
 CN 1705652 A 20051207 CN 2003-80101850 20031023
 MX 2005PA04183 A 20050608 MX 2005-PA4183 20050420
 US 2006058539 A1 20060316 US 2005-532096 20050421
 IN 2005CN00702 A 20070629 IN 2005-CN702 20050421
 PRIORITY APPLN. INFO.: DE 2002-10249378 A 20021023
 WO 2003-EP11736 W 20031023

L3 ANSWER 2 OF 6 CAPLUS COPYRIGHT 2008 ACS on STN

AB A continuous process for the epoxidn. of olefins
 (e.g., methyloxirane from propylene) with hydrogen peroxide using a
 product-stream predistn. step and unit is described and a process flow
 diagram presented.

ACCESSION NUMBER: 2001:581493 CAPLUS

DOCUMENT NUMBER: 135:137842

TITLE: Process for the epoxidation of
 olefins using a product-stream predistillation
 step and unit

INVENTOR(S): Hofen, Willi; Thiele, Georg; Moller, Alexander

PATENT ASSIGNEE(S): Degussa A.-G., Germany

SOURCE: Eur. Pat. Appl., 10 pp.

CODEN: EPXXDW

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 1122248	A1	20010808	EP 2000-102544	20000207
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO				
CA 2399129	A1	20010809	CA 2001-2399129	20010203
WO 2001057010	A1	20010809	WO 2001-EP1166	20010203
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
BR 2001008063	A	20021105	BR 2001-8063	20010203
EP 1254126	A1	20021106	EP 2001-911586	20010203
EP 1254126	B1	20030702		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
AT 244231	T	20030715	AT 2001-911586	20010203
JP 2003521544	T	20030715	JP 2001-556860	20010203
ES 2202281	T3	20040401	ES 2001-911586	20010203
ZA 2002005200	A	20030929	ZA 2002-5200	20020627
NO 2002003553	A	20020725	NO 2002-3553	20020725
US 2003114694	A1	20030619	US 2002-203184	20021004
US 6646141	B2	20031111		

PRIORITY APPLN. INFO.: EP 2000-102544 A 20000207
 WO 2001-EP1166 W 20010203

REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS

L3 ANSWER 3 OF 6 CAPLUS COPYRIGHT 2008 ACS on STN

AB Olefins with more than 3 carbon atoms can be epoxidated in liquid phase by molecular oxygen using as catalyst olefinic aldehydes, that give the corresponding olefinic acids, and sulfur or aromatic nitro derivatives. Thus: A solution of 168 g. acrolein, 420 g. propylene, 180 g. nitrobenzene, and 1170 g. EtOAc is poured into a pressure vessel, heated at 100°, and saturated with oxygen for 1 hr. The distillation of the solution gives 397.2 g. unreacted propylene, 69.3 g. acrylic acid, (64%) 84 g. unreacted acrolein, and 28.4 g. 1,2-epoxypropane (90%). A solution of 112 g. acrolein, 420 g. propylene, 1369 g. EtOAc, and 5 g. sulfur is heated at 80°, and treated with molecular oxygen 2 hrs. to give (with recyclization) 82% 1,2-epoxypropane, and 70% acrylic acid; without sulfur the yields are 15% and 70%, respectively. A solution of 210 g. methacrolein, 420 g. propylene, 180 g. nitrobenzene, and 1130 g. EtOAc is heated at 95° and treated with oxygen for 16 min. to give (with recyclization) 85% 1,2-epoxypropane, and 86% methacrylic acid, (conversions 7.6% and 28%, respectively). A solution of 210 g. crotonaldehyde, 420 g. propylene, 180 g. nitrobenzene, and 1130 g. EtOAc is heated at 90° and treated with oxygen for 25 min. to give (with recyclization) 91% 1,2-epoxy-propane, and 65% crotonic acid (conversions 5.8%, and 66%, respectively).

ACCESSION NUMBER: 1965:471400 CAPLUS

DOCUMENT NUMBER: 63:71400

ORIGINAL REFERENCE NO.: 63:13083f-h,13084a

TITLE: Epoxidation of olefins in liquid phase with molecular oxygen

INVENTOR(S): Lanos, Francoise; Clement, Genevieve

PATENT ASSIGNEE(S): Institut Francais du Petrole, des Carburants et Lubrifiants

SOURCE: 12 pp.

DOCUMENT TYPE: Patent

LANGUAGE: Unavailable

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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FR 1401176		19650521	FR	19630803
PRIORITY APPLN. INFO.:			FR	19630803

L3 ANSWER 4 OF 6 CAPLUS COPYRIGHT 2008 ACS on STN

AB The autoxidn. of allyl chloride (I), methallyl chloride (II), 1,4-dichlorobutene-2 (III), and 3,4-dichlorobutene-1 (IV) formed chlorohydrins by attack at the double bonds. Analysis of the initial products from II indicated an epoxide precursor was involved. Oxidation rates for III and IV were studied and show an unusual dependency on added anions. All allylic chlorides were fractionated. Oxidns. at atmospheric pressure were conducted using cylinder O. For pressure oxidns. an autoclave was used. Products from I and II were analyzed by gas chromatography. Without a catalyst the oxidation of II at 60° was very slow. A maximum oxidation rate of 5.5×10^{-7} mole O/ mole olefin/sec. was reached in 12 hrs.; after 44.7 hrs. 0.064 mole of O/mole II was consumed, and the reaction terminated. In order to obtain a higher conversion and allow isolation of products 90.6 g. II containing 1.8 g. cobaltic acetyl-acetonate and 5 g. cumene hydroperoxide oxidized 46.3 hrs. at 60° and distillation of an 89-g. aliquot of the liquid product gave 40.7 g., b200 35-7°, 5.9 g., b200 78-9° (contained 1.6 milliequiv. of epoxide), 2.5 g., b50 55-75°, 4.5 g. b10 66-90°. At 200 lb./sq. in. 487.1 g. II containing 20 g. MgO and 4.8 g. tert-butyl hydroperoxide oxidized at

100° with an off gas, the reaction terminated at 375 min. after the consumption of 3.55 moles of O, the solid product separated, dissolved in H₂O, washed, acidified, and extracted with Et₂O gave 9.8 g. of liquid consisting mainly of HCO₂H. The 510 g. of liquid oxidation product gave a min. of 15 separate peaks on gas chromatography. Chloroacetone and 1,3 - dichloro - 2 - methylpropanol-2 (V) constituted 24 and 11%, resp. Chloroacetone and 1,2-epoxy-3-chloro-2-methylpropane (VI) were identified by infrared gas spectra. V was purified by redistn., b₁₄ 62.8°, n_{20D} 1.4700, d₂₀ 1.250. The bis-2-naphthyl ether derivative m. 146-8°. Reaction with aqueous suspension of Ca(OH)₂ gave VI. Acidification of the salts yielded nearly all HCO₂H, a trace of AcOH, and no chloroacetic acid (43.2 min.). Attempts to titrate samples from various reaction stages for hydroperoxide iodometrically gave poor results. I (497.3 g.) containing 20 g. MgO at 100° and 200 lbs./sq. in. for 440 min. required 76.8 g. O and a constant maximum rate was reached in 260 min. ClCH₂CHO was identified. HCO₂H was present in the distillate. 1,3-Dichloropropanol was isolated as a pure liquid; phenylurethan m. 172-3°. The acid components (8.5 g.) extracted from the acidified MgO contained equal amts. of chloroacetic acid and HCO₂H. The oxidation of III at 90° was terminated after the consumption of 0.74 mole O at 27 hrs. Several tenths of a gram of (CO₂H₂) was directly filtered. The solution was found to contain 2.2 milliequiv./g. of acid. The solution, 81 g., taken up in CHCl₃, washed, dried, and distilled gave 13 g. unchanged III. No 1,3-isomer was obtained. Trichlorobutanol in 28% yield was collected at 68-77°/1 mm., n_{25D} 1.4980. The oxidation of 2M III in AcOH with 0.1M cobaltous chloride gave 0.19 mole HCl and 0.13 mole CO₂/mole of III. Distillation gave no separation of products. An 82% yield of a liquid b₃ 73-160° consisted of esters contaminated with acids, olefinic, and hydroxy compds. Titration of the crude oxidation mixture for hydroperoxide was unsuccessful. Oxidation of IV at 90° with 0.5% Co naphthenate consumed 0.16 mole O in 24 hrs., and purification of the product gave 35 g. IV and 7.6 g. III. No isomer was recovered for reaction in the absence of catalyst. The combined products from oxidation of 2M IV in AcOH representing 225 g. starting material were distilled. The AcOH forerun of 29 g. yielded an unstable 2,4-dinitrophenylhydrazone, m. 125°. From the 18.5 g. fraction, b₄ 54-66°, 4.5 g. crystals were obtained, m. 62-3°, probably ClCH₂CO₂H. The p-bromophenacyl ester m. 97-9°. The ester fraction, b₄ 72-81°, 14.5 g., on hydrolysis with 1% H₂SO₄ and steam distillation gave AcOH and a liquid from which 1,2,3,4-tetra- chlorobutane was obtained as platelets, m. 73°. The remaining liquid was trichlorobutanol; urethan m. 132-3°. The next highest boiling distillate, b₁ 81-127°, 8.6 g., appeared to be a mixture of esters. And the last fraction of 17 g., b_{1.1} 127° precipitated some crystals, m. 76-7°. The pot residue was 40.8 g. Pure 1,3,4-trichlorobutanol-2 (VII) was obtained by refluxing either the impure chlorohydrin or the ester fraction from the oxidation of III or IV with 5 times its weight of N MeOH-HCl. VII b₁ 80°, n_{25D} 1.5022.0 With base VII gave an epoxide, b₄₄ 96-100°, n_{20D} 1.4749; phenylurethan m. 132-3°. Reaction of the chlorohydrin with 20% NaOH gave 80% dichloroepoxybutane, b₁₀ 73-5°, n_{20D} 1.4767. The rate of basic hydrolysis of 0.1N chlorohydrin was second order rate. A plot of O consumed against time generally produced typical sigma shaped curves. The following results were obtained (isomer, solvent, temperature, concentration of the dichlorobutene, conen. of catalyst, added salt or acid,

and

the rate + 104 given): IV, AcOH, 90°: 2M, 0.1M, CoOAc, 10; 1M, 0.1M, CoOAc, 7.6; 2M, 0.05M, CoOAc, 7.8; 2M, 0.05M CoOAc, 0.015M HCl, 5.5; 2M, 0.05M, CoOAc, 0.2M, LiCl, 3.2; 2M, 0.05M, CoCl₂, 11. 3,4-Dichlorobutene, no solvent, 90°, no catalyst, 1.0, 0.5 mole-% Co as Co naphthenate, 3.2; 15 mole-% K₂CO₃, no reaction. CoOAc, and CoCl₂ represent cobaltous acetate-4H₂O and CoCl₂·6H₂O, resp. III, AcOH, 90°: 2M, 0.1M, CoOAc, 13; 2M 0.1M, CoOAc, 0.4M, Pb(OAc)₂, 26; 2M, -, CoCl₂, 30.100°: 2M, 0.1M, COCl₂, 23.80°: 2M, -, COCl₂,

21; 2M, 0.1M CoCl₂, 1% 2-azobisisobutyronitrile, 20.70°: 2M, 0.1M, CoCl₂, 8. III, no solvent, 90°: no catalyst, 10; 0.5 mole-% Co as Co naphthenate, 6.8, no catalyst, 1% 2-azobisisobutyronitrile, 10.80°: 0.5% Co as Co naphthcnate, 20%, light MgO, 11; no catalyst, 20%, light MgO 13. III, Me₃COH, 90°: 0.4M, negligible reaction.

ACCESSION NUMBER: 1962:1895 CAPLUS
DOCUMENT NUMBER: 56:1895
ORIGINAL REFERENCE NO.: 56:300g-i,301a-i,302a
TITLE: Autoxidation of liquid allylic chlorides
AUTHOR(S): Brill, Wm. F.
CORPORATE SOURCE: Food Machinery and Chem. Corp., Princeton, NJ
SOURCE: Journal of Organic Chemistry (1961), 26, 2969-72
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L3 ANSWER 5 OF 6 CAPLUS COPYRIGHT 2008 ACS on STN

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 50, 2412i. Me₂CHC(OH)Ph₂ (I) gave 60% Me₂C:CPh₂ (II) with Ac₂O and 50% with o-C₆H₄(CO)₂O (IIa); it was best prepared by keeping 40 g. I, 50 g. C₅H₅N, and 42 g. POCl₃ at room temperature several days, pouring on ice, extracting with Et₂O, drying the exts., concentrating, distilling, refluxing the distillate 6 hrs. with Na, and redistg. to give pure II, b1.6 114°, n_D²⁰ 1.586. II (20 g.) in 100 cc. Ac₂O treated in 0.5 hr., with cooling, with 15 g. Cr₂O₃ in 80 cc. Ac₂O, stirred 3 hrs., poured into 1.5 l. H₂O, and the product extracted with Et₂O gave 14.4 g. CMe₂.CPh₂.O (III), b0.7 102-12°, m. 64° (alc.); by-products of the reaction were identified as Ph₂CO and Me₂CO. II and Bz₂O₂ also gave III, b0.25 88°. III (0.2 g.) and 5 cc. 43% H₂SO₄ shaken several days gave a diol, m. 94-5° (petr. ether). II reacted vigorously with Cr₂O₃ in 65% H₂SO₄, giving no III, but instead, Ph₂CO and Me₂CO. p-MeC₆H₄CH(OH)CHMe₂ and saturated Et₂O-HCl gave p-MeC₆H₄CHClCHMe₂ which, treated in situ, with C₅H₅N gave p-MeC₆H₄C:CMe₂ (IV), m. 58-9° (alc.). As above, 20 g. IV and 11 g. Cr₂O₃ in Ac₂O gave 13 g. epoxide (V), b1.5-1.7 139-42° [by-products were (p-MeC₆H₄)₂CO and Me₂CO]; IV and Bz₂O₂ also gave V, m. 58-9°. V, as above gave a diol, identified by oxidation with HIO₄ to (p-MeC₆H₄)₂CO (VI). IV and Cr₂O₃ in 43% H₂SO₄ gave VI but no V. p-BrC₆H₄MgBr (from 500 g. p-BrC₆H₄Br and 60 g. Mg) and 110 g. Me₂CHCO₂Et gave crude (p-BrC₆H₄)₂C(OH)CHMe₂ (VII); distillation of VII gave (p-BrC₆H₄)₂C:CMe₂ (VIII), b0.7 174°, m. 97° (alc.); as above, 15 g. VIII gave 10 g. epoxide (IX), b1.2 177-8°, m. 94-5° (alc.); IX was unaffected by 43% H₂SO₄ at room temperature for 3 days. Similarly were prepared (p-ClC₆H₄)₂C(OH)CHMe₂, (p-ClC₆H₄)₂C:CMe₂, b0.2 132°, m. 71-2°, and the epoxide (X), b0.65 148-50°, m. 57-8°. Me₂CHCHMeC(OH)Ph₂, b2 198-200°, n_D¹⁷ 1.564, (205 g.) and 600 g. IIa gave Me₂CHCMe:CPh₂ (XI), b15 168-70°, n_D¹⁵ 1.5740 and X gave the epoxide (XII), b12 172-4°, m. 93° (alc.); XII also resisted hydrolysis with 43% H₂SO₄. Me(iso-Pr)C(CO₂Et)₂ gave Me₂CHCHMeCO₂H, b. 142-6°, n_D²⁰ 1.4023.

ACCESSION NUMBER: 1958:25393 CAPLUS
DOCUMENT NUMBER: 52:25393
ORIGINAL REFERENCE NO.: 52:4561g-i,4562a-b
TITLE: Reactions of unsaturated compounds. XIII. Oxidation of 1,1-diarylelefins by chromic oxide
AUTHOR(S): Hickinbottom, W. J.; Moussa, G. E. M.
CORPORATE SOURCE: Univ. London
SOURCE: Journal of the Chemical Society (1957) 4195-8
CODEN: JCSOA9; ISSN: 0368-1769
DOCUMENT TYPE: Journal

LANGUAGE:

Unavailable

L3 ANSWER 6 OF 6 CAPLUS COPYRIGHT 2008 ACS on STN

AB The object of this work was the preparation and study of the phys. properties of certain hydrocarbons with b. ps. in the range of gas oil (petroleum) fraction b. 200-320°. Preparation of hydrocarbons: Aliphatic series: (1) Pentadecane (I). Condensation of $(\text{CH}_2\text{O})_3$ with $\text{C}_6\text{H}_{13}\text{MgBr}$ gave 38% heptanol; condensation of $\text{C}_7\text{H}_{15}\text{MgBr}$ with HCO_2Et gave 61% 8-pentadecanol (II), m. 43.5° (from $\text{EtOH-H}_2\text{O}$), b11 153° (cf. C.A. 41, 5850e for data on $\text{C}_6\text{H}_{13}\text{Br}$ and $\text{C}_7\text{H}_{15}\text{Br}$). Dehydration of II in H_2SO_4 gave 7-pentadecene, b20 137°, d20 0.7726, n20D 1.4370, MR (mol. refraction) 71.21, oxidation of which with $\text{CrO}_3\text{-HOAc}$ yielded heptanoic acid, b. 218-24°, and octanoic acid, b. 233-8°, both characterized by titration and the Ag salts. Catalytic hydrogenation with Pt black of II gave I, b22 145°, d20 0.7638, n20D 1.4286, MR 71.49. (2) 4,6-Dipropylnonane could not be prepared The 4-heptanol (III) prepared in 88% yield from $\text{C}_3\text{H}_7\text{MgBr}$ and HCO_2Et b25 70°, d20 0.8127, n20D 1.4184, MR 36.00; these data compared favorably with those for III prepared from $\text{C}_3\text{H}_7\text{MgBr}$ and $\text{C}_3\text{H}_7\text{CHO}$, in contrast to the poorer data for III prepared from esters: b25 64°, d20 0.8139, n20D 1.4181, MR 35.92. The $\text{C}_7\text{H}_{15}\text{MgBr}$ was formed with difficulty, EtBr being necessary to prime the reaction, and subsequent condensation with HCO_2Et gave only secondary products, notably 2-propyl-1-pentanol. The preparation of 3-propyl-2-(2-propylbutyl)hexanoic acid (IV) by malonic ester synthesis (for subsequent decarboxylation to $\text{C}_{15}\text{H}_{32}$) was unsuccessful. (3) 2,4,8,10-Tetramethylhendecane could not be prepared from $\text{Me}_2\text{CHCH}_2\text{CHMeCH}_2\text{MgBr}$ and HCO_2Et ; only secondary products were obtained. 4-Methyl-2-pentanol, 81% from $\text{Me}_2\text{CHCH}_2\text{MgBr}$ and AcH , b10 47°, d20 0.80708, n20D 1.4101, MR 31.22; formation of its bromide with P and Br or with HBr was difficult, and subsequent condensation with $(\text{CH}_2\text{O})_3$ gave mostly secondary products and 8% 2,4-dimethylpentanol. (4) 2,6-Dimethyl-3,5-diisopropylheptane was not formed from $(\text{Me}_2\text{CH})_2\text{CHMgBr}$ and HCO_2Et , but instead $(\text{Me}_2\text{CH})_2\text{CH}_2$, $\text{Me}_2\text{CHCH:CMe}_2$, and $(\text{Me}_2\text{CH})_2\text{CHCH}_2\text{OH}$ were obtained. The malonic ester synthesis was considered improbable after attempted preparation of IV. (5) Hexadecane (V), 60% from 1-bromooctane and Na, b11 153°, d20 0.7770, n20D 1.4351, MR 75.91; in Et_2O the reaction is slow, with an intermediate blue color; if 1-bromooctane is added to a suspension of Na in xylene, the initially fast solution of the Na is followed by the slow elimination of Br as NaBr (refluxing 3 h.) (70% yield). (6) 5-Methyl-4,6-dipropylnonane. The intermediate $(\text{Pr}_2\text{CH})_2\text{C}(\text{OH})\text{Me}$ could not be obtained by Grignard condensation, only secondary products such as 3-propyl-2-hexanol. (7) 4,7-Dipropyldecane (VI). 4-Heptanone (VII), from 4-heptanol and $\text{CrO}_3\text{-HOAc}$, b741 142°, d20 0.8116, n20D 1.4065, MR 34.53; semicarbazone m. 135°. $\text{BrMgC.tplbond.CMgBr}$ (VIII) was made by passing a stream of pure C_2H_2 into Et_2O and EtMgBr until C_2H_6 evolution ceased and 2 liquid layers appeared; condensation with VII gave 89% acetylenic glycol, m. 120° (from CCl_4), dehydration of which in boiling 25% H_2SO_4 gave 4,7-dipropyl-3,7-decadien-5-yne (IX), b25 142°, d20 0.8111, n20D 1.4862, MR 77.19 (an extraordinary exaltation of 4.04 was noted). Hydrogenation with Pt black gave VI with phys. data different from those found in the literature (cf. C.A. 8, 1579), b23141°, d20 0.7802, n20D 1.4350, MR 75.59. Selective hydrogenation with Raney Ni in EtOH gave instead intermediate products, identified by oxidation: 4,7-dipropyl-3,5,7-decatriene, 4,7-dipropyl-4,6-decadiene, and 4,7-dipropyl-5-decene. (8) 2,4,6,8,10-Pentamethylhendecane. An attempted preparation by Grignard condensation of $\text{Me}_2\text{CHCH}_2\text{CHMeCH}_2\text{Br}$ with EtOAc gave only secondary products, such as 2,4-dimethyl-6-hexanol, 2,4-dimethyl-1-pentene, and 2,4-dimethylpentane. (9) 2,4,6-Trimethyl-3,5-diisopropylheptane could not be prepared by Grignard condensation of $(\text{Me}_2\text{CH})_2\text{CHBr}$ (C.A. 41, 5850e) with EtOAc . (10) 2,7-Dimethyl-3,6-diisopropyloctane (X). $(\text{Me}_2\text{CH})_2\text{CO}$, formed by CrO_3 oxidation of the alc., was condensed with VIII to 2,7-dimethyl-3,6-diisopropyl-4-

octyne-3,6-diol, m. 109° (from CCl₄); the condensation of this ketone, doubly branched in the α -position, goes normally. Dehydration in 20% H₂SO₄ gave 2,7-dimethyl-3,6-diisopropyl-2,6-octadien-4-yne (XI), b₂₈ 142°, d₂₀ 0.8360, n_{20D} 1.5050, MR 77.34. Catalytic hydrogenation with Raney Ni at 180° and 120 kg./sq. cm. gave X, b₃₅ 142°, d₂₀ 0.7968, n_{20D} 1.4470, mol. refraction 75.78; hydrogenation with Pt black gave instead 2,7-dimethyl-3,6-diisopropyl-4-octene (XII), b₂₁ 132°, d₂₀ 0.8157, n_{20D} 1.4513, MR 73.99; hydrogenation with Raney Ni (room temperature and 1 atmospheric) gave intermediate products, 2,7-dimethyl-3,6-diisopropyl-2,4,6-octatriene, and 2,7-dimethyl-3,6-diisopropyl-3,5-octadiene, as well as XII. (11) 5,8-Dibutyldodecane (XIII). BuMgBr and HCO₂Et gave 92% 5-nonanol, b₂₇ 103°, d₂₀ 0.8257, n_{20D} 1.4289, MR 44.95, oxidized with CrO₃ to 5-nonanone; condensation with VIII gave 83% 5,8-dibutyl-6-dodecyne-5,8-diol, m. 130.5° (from EtOH). Dehydration in 25% H₂SO₄ gave 5,8-dibutyl-4,8-dodecadien-6-yne (XIV), b₂₉ 189°, d₂₀ 0.8222, n_{20D} 1.4866, MR 95.77; total hydrogenation with Pt black in HOAc yielded XIII, b₃₂ 192°, d₂₀ 0.7922, n_{20D} 1.4436, MR 94.48. Hydrogenation with Raney Ni in EtOH gave intermediate compds. (12) 2,9-Dimethyl-4,7-diisobutyldecane (XV), prepared similarly to XIII in 81% yield, b₃₀ 167°, d₂₀ 0.7882, n_{20D} 1.4412, MR 94.52. 2,9-Dimethyl-4,7-diisobutyl-5-decyne-4,7-diol, m. 72° (from ligroin), was dehydrated in 25% H₂SO₄ to 2,9-dimethyl-4,7-diisobutyl-3,7-decadien-5-yne (XVI), b₂₈ 156°, d₂₀ 0.8023, n_{20D} 1.4783, MR 95.94. Total hydrogenation to XV was possible only at a pressure of 130 kg./sq. cm. at 180° with Raney Ni. (13) The Wurtz reaction gave very poor yields of the desired hydrocarbons; the main products were dimers and "intermol. rearrangement" products of free radicals. Condensation of 1-bromodecane and iso-AmBr in Bu₂O with Na gave a small quantity of impure 2-methyltetradecane, b₂₂ 152°, d₂₀ 0.7832, n_{20D} 1.4290, MR 71.75; the main products were Me₂CHEt, the 2-methylbutenes, and the dimer of the decyl radical, eicosane. Instead of 2methyl-4-isobutyldecane from 1-bromohexane and (Me₂CHCH₂)CHBr, only secondary products such as dodecane were formed. Tetradecane (XVII), and not the desired 2-methyl-4-isobutylhendecane, was the main product from 1-bromoheptane and (Me₂CHCH₂)₂CHBr, b₂₃ 135°, d₂₀ 0.7700, n_{20D} 1.4303, MR 66.46. PrCHBrCH₂CHMe₂ and Na in xylene gave only "intermol. rearrangement" products and not the desired dimer, 2,7-dimethyl-4,6-dipropyloctane. Arylaliph. series: (1) 1,2-Diphenylethane (XVIII). 1,2-Diphenylethanol, from PhCH₂MgCl and BzH, m. 69° (from CCl₄); dehydration in 50% H₂SO₄ gave stilbene, m. 124° (from EtOH), and hydrogenation with Raney Ni easily formed XVIII, m. 52°. (2) 1,1-Diphenylpropane (XIX). 1,1-Diphenyl-1-propanol (XX), in 87% yield from EtMgBr and PhBz, m. 96° (from 90% EtOH) [cf. Klages, Ber. 35, 2647 (1902)], was dehydrated by distillation in vacuo with activated clay to 1,1-diphenyl-1-propene, b₁₅ 154°, d₂₀ 1.0250, n_{20D} 1.5880, MR 63.70; hydrogenation with Raney Ni gave XIX, b₁₈ 145°, d₂₀ 0.9975, n_{20D} 1.5701, MR 64.48. Dehydration of XX in boiling EtOH easily gave the dimer 2,3-dimethyl-1,1,4,4-tetraphenyl-1-butene, m. 212°; the structure was determined by Br number, mol. weight by f.p. in C₆H₆, and oxidation (3) 1,2-Diphenylpropane (XXI). PhCH₂MgCl and AcPh gave 92% 1,2-diphenyl-2-propanol, m. 72° (from EtOH), b₉ 163°, dehydrated in boiling 50% H₂SO₄ to 1,2-diphenyl-2-propene, m. 81° (from EtOH), b₂₂ 170°, slightly soluble in Et₂O. Hydrogenation with Pt black was selective, to form XXI, b₂₅ 160°, d₂₀ 0.9799, n_{20D} 1.5573, MR 64.42. (4) 1,3-Diphenylpropane (XXII). PhCH₂MgCl and HCO₂Et gave only 7-8% 1,3-diphenyl-2-propanol (XXIII), owing to the formation of secondary products such as PhCH₂CH₂OH; the Grignard condensation of PhCH₂CH₂Br with BzH gave 35% 1,3-diphenyl-1-propanol (XXIV), m. 71° (from EtOH), b₁₄ 186°. Dehydration of XXIII with H₂SO₄ gave trans-1,3-diphenylpropene, m. 51° (from EtOH), b₂₅ 159°; similarly XXIV gave a mixture, b₁₅ 170°, d₂₀ 0.9978,

n20D 1.5689, MR 63.68; chilling removed 30% as the solid trans form, and the oily liquid was purified to cis-1,4-diphenylpropene, b18 178°, d20 1.0138, n20D 1.5807, MR 63.75. XXII, formed by hydrogenation with Raney Ni of either isomer, b18 160°, d20 0.9831, n20D 1.5594, MR 64.41. (5) 1,2-Diphenylbutane (XXV), b28 172°, d20 0.9777, n20D 1.5554, MR 68.98. Friedel-Crafts condensation of EtCOCl and C6H6 gave 88% Et Ph ketone, b11 97°, d20 1.0103, n20D 1.5256, MR 40.69, which with PhCH2MgCl gave 1,2-diphenyl-2-butanol, b20 180°, d20 1.0367, n20D 1.5752, MR 72.06. Dehydration in H2SO4 or P2O5 gave a mixture of isomeric olefins; subsequent hydrogenation with Raney Ni was selective, to form XXV, attacking only isomers without a double bond between the 2 rings (the formation of XVIII from stilbene is an exception to this general rule). (6) 1,4-Diphenylbutane (XXVI). The 2 diastereoisomers of 1,4 diphenyl-2-butyne-1,4-diol, from BzH and VIII, were separated by their different solubilities in Et2O; on crystallization from EtOH the α -form m. 146° and the β -form m. 99.5°. The products, predominantly α -, resinify easily in acid. Hydrogenation gave the stereoisomeric diols; α -form (XXVII) of 1,4-diphenyl-1,4-butanediol m. 110°; β -form m. 93°. In contrast to the aliphatic diols, dehydration of XXVII with 30% H2SO4 did not give a diolefin, but instead 1,4-diphenyl-1,4-epoxybutane (2,5-diphenyltetrahydrofuran) (XXVIII), b27 210°, d20 1.0752, n20D 1.5770, MR 63.49, very stable, resistant to H in EtOH with Raney Ni or Pt black, reacts slowly with H and Pt black in HOAc. In contrast, the action of nascent H, from Na and EtOH, is very effective, giving 1,4-diphenyl-1-butanol, b32 218°, d20 1.0347, n20D 1.5553, MR 65.17; dehydration in 60% H2SO4 then gave 1,4-diphenyl-1-butene, b14 170°, d20 1.0330, n20D 1.5945, MR 68.37. The XXVI produced by hydrogenation with Raney Ni, m. 52.5°, was identical with that prepared from PhCH2CH2Br and Na. No rearrangement occurred in the dehydration of XXVII (cf. Tiffeneau, Orekhoff, and Levy, C.A. 26, 2429). (7) 1,2-Diphenylpentane (XXIX), b32 184°, d20 0.9649, n20D 1.5480, MR 73.74. 1,2-Diphenyl-2-pentanol, 94% from PhCH2MgCl and PrBz, b22 184°, d20 0.9913, n20D 1.5882, MR 81.50, was dehydrated with H2SO4 to a mixture (XXX) of isomeric olefins, b27 185°, d20 0.9868, n20D 1.5798, MR 74.85; dehydration with P2O5 gave a mixture (XXXI), b28 196°, d20 1.0026, n20D 1.5807, MR 73.76. XXXI contains mostly 1,2-diphenyl-2-pentene and is smoothly hydrogenated at normal pressure with Raney Ni to XXIX, whereas XXX, containing mostly 1,2-diphenyl-1-pentene, is not hydrogenated. (8) 2,5-Diphenylhexane (XXXII). 2,5-Diphenyl-3-hexyne-2,5-diol, from VIII and MeBz, was separated into the α -form, m. 163.5° (from EtOH), and the predominant β -form (XXXIII), m. 126° (from C6H6), by the virtual insolvency of the α -form in Et2O. Attempted dehydration caused resin formation, especially with XXXIII and 10% H2SO4, when a red resin was obtained. So hydrogenation gave 2,5-diphenyl-2,5-hexanediol as the α -form (XXXIV), m. 158.5°, and the β -form, m. 136°; dehydration of XXXIV in 20% H2SO4 gave (as with XXVII above) 2,5-diphenyl-2,5-epoxyhexane (2,5-dimethyl-2,5-diphenyltetrahydrofuran) (XXXV), b29 202°, d20 1.0380, n20D 1.5637, MR 73.29. The resistance of XXXV to catalytic hydrogenation was analogous to that of XXVIII; rupture of the heterocyclic ring with Na and EtOH gave 2,5-diphenyl-2-hexanol, b20 202°, d20 1.0125, n20D 1.5468, MR 74.52. Dehydration with 50% H2SO4 gave 2 olefins: a solid form, m. 139° (from EtOH), and a liquid, b12 183°, d20 0.9916, n20D 1.5659, MR 77.62 (possible stereoisomers of 2,5-diphenyl-2-hexene) [cf. Klages, Ber. 35, 2633(1902), and C.A. 1, 3005]. Attempted hydrogenation of these olefins with Raney Ni did not form the desired XXXII, but instead cyclization gave trans-1,2-dimethyl-1,2-diphenylcyclobutane (XXXVI), b16 172°, m. 52.5°, and the cis-form (XXXVII), b16 172°, d20 0.9961, n20D 1.5540, MR 75.93; this reaction will be

investigated further with larger amts. of starting material. (9) 1,1,2-Triphenylethane (XXXVIII). Dehydration of $\text{Ph}_2\text{C}(\text{OH})\text{CH}_2\text{Ph}$ (triphenylethanol) (82% from PhBz and PhCH_2MgCl , m. 89°) with AcCl gave $\text{Ph}_2\text{C}:\text{CHPh}$, triphenylethylene, m. 73° , and hydrogenation with Na and AmOH then gave the desired XXXVIII, m. 54.5° . Cyclic series: (1) Decylcyclohexane (XXXIX). Catalytic hydrogenation of phenyldecane, 10% from 1-bromodecane, C_6H_6 , and AlCl_3 , b₁₄ 158° , d₂₀ 0.8978, n_{20D} 1.5078, MR 72.36, with Pt black was strongly inhibited, apparently by traces of AlCl_3 . BzH and $\text{C}_9\text{H}_{19}\text{MgBr}$ gave 50% 1-phenyl-1-decanol, m. 34° (from EtOH), b₁₇ 189° , crystals greasy to the touch; equimol. amts. of PhCH_2OH and C_9H_{18} were also formed. Dehydration with H_2SO_4 gave 1-phenyl-1-decene, b₂₆ $183-4^\circ$, d₂₀ 0.8726, n_{20D} 1.4878, MR 71.29, hydrogenation of which then gave the desired XXXIX, b₂₀ 168° , d₂₀ 0.8167, n_{20D} 1.4520, MR 73.98. The hydrogenation was selective, the intermediate phenyldecane being insol. in HOAc ; the reaction then continued at 25% of the original rate. (2) 1,4-Diphenylcyclohexane could not be formed from $\text{C}_5\text{H}_{11}\text{I}$ and $p\text{-Br}_2\text{C}_6\text{H}_4$ with Na ; only C_5H_{12} , C_5H_{10} , $\text{C}_{10}\text{H}_{22}$, and dimethyloctane were formed. The condensation of $\text{C}_5\text{H}_{11}\text{MgBr}$ with $p\text{-Br}_2\text{C}_6\text{H}_4$ with FeCl_3 (cf. C.A. 39, 2739.6) was also unsuccessful. (3) 1,2-Dicyclohexylethane (XL), obtained by the hydrogenation at 180° with Raney Ni of $\text{PhCH}_2\text{CH}(\text{OH})\text{Ph}$, b₁₉ 140° , d₂₀ 0.8825, n_{20D} 1.4802, MR 62.47. (4) 1,1-Dicyclohexylpropane (XLI), from $\text{Ph}_2\text{CHCH}_2\text{CH}_2\text{OH}$ by hydrogenation with Raney Ni, b₁₄ 131° , d₂₀ 0.9023, n_{20D} 1.4935, MR 67.05. Condensation of EtCO_2Et and $\text{C}_6\text{H}_{11}\text{MgCl}$ gave only secondary products: C_6H_{12} , C_6H_{10} , $\text{C}_6\text{H}_{11}\text{CH}_2\text{Ac}$, and cyclohexylpropanol. (5) 1,2-Dicyclohexylpropane (XLII), from the hydrogenation of $\text{PhCH}_2\text{CHPhMe}$ with Pt black, b₁₅ 148° , d₂₀ 0.8819, n_{20D} 1.4791, MR 66.90. (6) 1,3-Dicyclohexylpropane (XLIII), from the hydrogenation of $\text{PhCH}_2\text{CH}:\text{CHPh}$ in HOAc with Pt black, b₂₄ 151° , d₂₀ 0.8740, n_{20D} 1.4750, MR 67.01; the hydrogenation was nonselective, acting equally on the olefinic bond and the aromatic nuclei. (7) 1,2-Dicyclohexylbutane (XLIV), obtained from $\text{PhCH}_2\text{C}(\text{OH})\text{PhEt}$ by hydrogenation with Raney Ni at 185° , b₂₂ 160° , d₂₀ 0.9146, n_{20D} 1.5038, MR 71.85. (8) 1,4-Dicyclohexylbutane (XLV), obtained similarly from $[\text{CH}_2\text{CH}(\text{OH})\text{Ph}]_2$ at 180° , b₁₉ 167° , d₂₀ 0.8731, n_{20D} 1.4758, MR 71.69. (9) 1,2-Dicyclohexylpentane (XLVI), prepared similarly from $\text{PhCH}_2\text{C}(\text{OH})\text{PhPr}$, b₁₇ 157° , d₂₀ 0.9218, n_{20D} 1.5092, MR 76.47. (10) 2,5-Dicyclohexylhexane (XLVII), from $[\text{CH}_2\text{C}(\text{OH})\text{PhMe}]_2$, b₃₂ 201° , d₂₀ 0.8901, n_{20D} 1.4876, MR 80.87. (11) 1,1,2-Triphenylethanol was hydrogenated to 1,1,2-tricyclohexylethane (XLVIII), b₃₀ 230° , d₂₀ 1.0236, n_{20D} 1.5786, MR 90.21. Studies of hydrocarbon properties as a function of mol. structure: Generally the aliphatic hydrocarbons show increasing d. and n with increase in branching; the b. ps. decrease. The polyolefinic hydrocarbons show a trend in d. and n with the C/H ratio or degree of unsatn. The mol. exaltation due to the acetylenic group is roughly 3 times that for ethylenic bonds. The following phys. data (see also under each of the preceding individual syntheses), i.e., the mol. exaltation (observed mol. refraction - calculated value), the kinematic

viscosity

in centistokes, and the absolute viscosity in centipoises, are given: XVII, -0.42, 3.45, 2.66; I, -0.01, 3.75, 2.35; V, -0.21, 4.33, 3.37; VI, -0.53, 3.71, 2.90; IX, -0.34, 4.65, 3.71; XI, -0.12, 10.28, 8.14; XII, -0.08, 9.64, 7.60; for the following only the mol. exaltation is given: IX, +4.04; XI, +4.19; XIV, +4.11; 5,8-dibutyl-4,6,8-dodecatriene, +2.02; 5,8-dibutyl-5,7-dodecadiene, +1.01; XVI, +4.28; 2,9-dimethyl-4,7-diisobutyl-3,5,7-decatriene, +2.16; 2,9-dimethyl-4,7-diisobutyl-4,6-decadiene, +1.02. The phys. state of the arylaliph. hydrocarbons is intimately bound to the mol. structure especially the degree of symmetry.

Asym.

compds. are liquid whereas the sym. ones are solid. The d. and n of liqs. decrease with increasing chain length (or decrease in C/H ratio) and with

increasing degree of symmetry. Phys. data (read as above): XIX, +0.18, 5.07, 5.06; XXI, +0.12, 6.74, 6.61; XXII, +0.15, 7.81, 7.83; XXV, +0.06, 9.36, 9.15; XXIX, +0.20, 12.00, 11.58. With the cyclic hydrocarbons, the d. and n of the sym. isomers are lower than of the asym. ones. Phys. data (read as above): XXXIX, +0.05, 6.14, 5.01; XL, -0.01, 7.90, 6.96; XLI, -0.05, 9.68, 8.74; XLII, -0.20, 11.52, 10.16; XLIII, -0.09, 8.91, 7.80; XLIV, +0.13, 10.99, 10.05; XLV -0.03, 12.71, 11.17; XLVI, +0.13, 14.68, 13.53; XLVII, -0.09, 23.35, 20.79; XLVIII, 0.00, 122.85, 127.80; XXXVI, m. 52.5°, b16 166°; XXXVII, b16 172°, -0.03, 41.56, 41.40. The viscosity of the 3 series above at 20° increases with the length of C chain, but not with the C/H ratio; the arylaliph. asym. hydrocarbons have lower values than the corresponding cyclic compds. An increase occurs with the appearance of closed rings, also with degree of symmetry for compds. of analogous structure. More evidence is needed to confirm these generalities. Conclusions: (1) The Wurtz reaction does not go so simply as given in the standard texts; free radicals play an important part. Temperature is important, especially in the isomerization of the radicals, and it is difficult to isolate pure products, due to secondary products. (2) The Grignard condensation is a better method for obtaining the desired structures, with min. rearrangement of the reactants. (3) Dehydration and dehydrogenation depend greatly on mol. structure; the acetylenic diols dehydrate differently in the aliphatic and arylaliph. series. After removal of the triple bond, epoxides are formed. Compds. of the type ArCH:CRAr are resistant to catalytic hydrogenation, so that selective reduction to arylaliph. or to cyclic hydrocarbons can be accomplished. Similarly, acetylenic diols are also selectively hydrogenated; the partial reduction of the triple bond is characterized by (1) a slower reaction, (2) change from exothermic to endothermic reaction, and (3) precipitation of the insol. olefin from EtOH. The hydrogenation of the sym. diaryl 1,4-epoxides is free of intramol. rearrangement.

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4045 COMPRESS
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AB Ethylene (I) and propylene (II) are separated from the raw gas, formed from pyrolysis of hydrocarbons, by washing the raw gas at 8-12 atmospheric with a N-alkyl-γ- or δ-lactam to dissolve acetylenes, diolefins, H₂S, S-containing organic compds. and C₄ hydrocarbons. The washed gas contains I, II,
H₂S, CO, H, CH₄, CO₂, ethane, propane, and butane. Preferred

lactam for washing is N-methylpyrrolidinone (III). The washed gas is treated with an aqueous alkali solution to remove traces of H₂S and CO₂. The purified gas is compressed to 25-35 atmospheric, and either condensed by cooling it at very low temperature, or absorbed by a liquid. The condensate or the solution is distilled to give pure I and II. The components absorbed by III, namely, acetylene, diolefins, H₂S, S-containing organic compds. and a part of CO₂, are regenerated by evaporation. The regenerating column is a continuous distillation column, fed with the washing liquor and with steam at such a rate that at the head of the column a part of water and the regenerated components are distilled. The III in the residue contains 1-10% water. The hot residual III is dehydrated by bubbling through it a part of CH₄ and of H₂, released in the purification. Acetylene and diolefins are partly polymerized during the regeneration. The consumption of alkali is low. A design of the plant is given.

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 DOCUMENT NUMBER: 65:19864
 ORIGINAL REFERENCE NO.: 65:3649f-h
 TITLE: Separation of ethylene and propylene from raw
 pyrolyzed gas
 INVENTOR(S): Thormann, Kurt
 PATENT ASSIGNEE(S): Metallgesellschaft A.-G.
 SOURCE: 5 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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DE 1183902		19641223	DE 1960-M45718	19600623
PRIORITY APPLN. INFO.:			DE	19600623

L4 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2008 ACS on STN

AB The process of U.S. 2,-600,110 (CA 46, 8358h), which is based on the heat-pump principle, is improved by passing a major portion of the compressed vapors of the kettle product refrigerant to the kettle section of the fractionator and compressing the rest of the vapors in a 2nd compression step so that they are condensed by available cooling water, thus increasing the efficiency of heat transfer. The improved process is particularly adapted to the separation of C₂H₄ from C₂H₆, C₃H₆ from C₃H₈, and C₄H₈ from C₄H₁₀.

ACCESSION NUMBER: 1966:57911 CAPLUS
 DOCUMENT NUMBER: 64:57911
 ORIGINAL REFERENCE NO.: 64:10793d-e
 TITLE: Fractional distillation
 INVENTOR(S): Palen, Joseph W.; Moon, John J.
 PATENT ASSIGNEE(S): Phillips Petroleum Co.
 SOURCE: 5 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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US 3229471		19660118	US 1961-160066	19611218
PRIORITY APPLN. INFO.:			US	19611218

L4 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2008 ACS on STN

AB A normally gaseous hydrocarbon component is separated from a mixture of normally gaseous hydrocarbons by introducing the mixture into a distillation

zone. A bottom fraction and a vaporous overhead fraction are withdrawn from the distillation zone. A portion of the overhead fraction, which comprises the component which is to be separated, is compressed and thereby heated. A portion of the compressed overhead fraction, which has been further heated or cooled, is brought into contact indirectly with liquid from the lower portion of the distillation zone thereby heating and partially vaporizing the liquid from the distn . zone and partially condensing the overhead. The condensed overhead may be used to reflux the distillation zone, while the vaporized liquid may be used to reboil the distillation zone. This process may be used in the separation of C₂H₄ from C₂H₆ in a C₂-splitting operation or for the separation of C₃H₆ from C₃H₈.

ACCESSION NUMBER: 1962:455562 CAPLUS
 DOCUMENT NUMBER: 57:55562
 ORIGINAL REFERENCE NO.: 57:10979a-c
 TITLE: Gas separation, especially in production of ethylene and propylene
 INVENTOR(S): Greco, Saverio G.
 PATENT ASSIGNEE(S): M. W. Kellogg Co.
 SOURCE: 6 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3000188		19610919	US 1956-622291	19561115
PRIORITY APPLN. INFO.:			US	19561115

L4 ANSWER 4 OF 4 CAPLUS COPYRIGHT 2008 ACS on STN

AB Isobutane (60-90 volume % of the hydrocarbon charge) and olefins, such as propene, react in the liquid phase in the presence of a nonvolatile alkylation catalyst, e.g. H₂SO₄ (88-94 weight % titratable acidity). The temperature and pressure conditions (30-75°F. and 0-30 lb./sq. in. gage) are such that part of the isobutane and practically all of the C₃H₈ and lighter products are evaporated to give effective refrigeration for the alkylation zone. The alkylator delivers a depropanized liquid emulsion to be settled and caustic-washed free of acid. This alkylate passes to the top of a distillation tower where butanes are distilled from the downcoming alkylate and returned to the alkylator. The isobutane-rich vapors from the alkylator containing C₃H₈ are compressed (40-130 lb./sq. in. gage) and condensed with cooling water. The condensate is depropanized, and the isobutane-rich bottoms are returned to the alkylator.

ACCESSION NUMBER: 1962:443938 CAPLUS
 DOCUMENT NUMBER: 57:43938
 ORIGINAL REFERENCE NO.: 57:8811f-h
 TITLE: Catalytic alkylation of olefins with isobutane
 PATENT ASSIGNEE(S): Texaco Development Corp.
 SOURCE: 9 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 895178		19620502	GB 1960-15908	19600505
PRIORITY APPLN. INFO.:			US	19590511

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COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

53.46

53.67

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE

TOTAL

ENTRY

SESSION

CA SUBSCRIBER PRICE

-8.00

-8.00

SESSION WILL BE HELD FOR 120 MINUTES

STN INTERNATIONAL SESSION SUSPENDED AT 19:50:38 ON 25 MAR 2008